Supporting Information

Three-Dimensional Au Microlattices as Positive Electrodes for Li-O_2 Batteries

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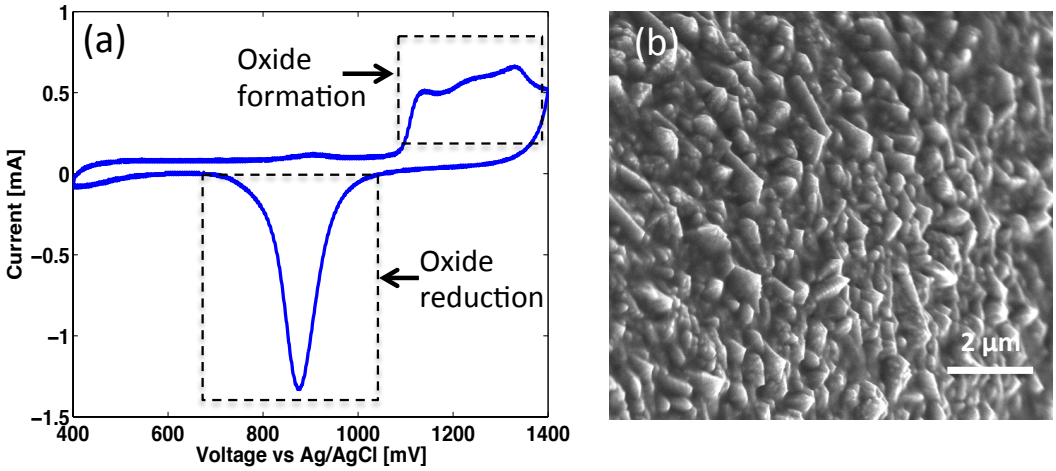

Figure S1. Cyclic voltammogram of as-fabricated Au microlattice and SEM of the surface of the sample. (a) CV of hollow Au microlattice in 0.5 M H_2SO_4 with a scan rate of 50 mV s^{-1}; (b) SEM image of rough polycrystalline Au surface obtained via constant current electrodeposition.

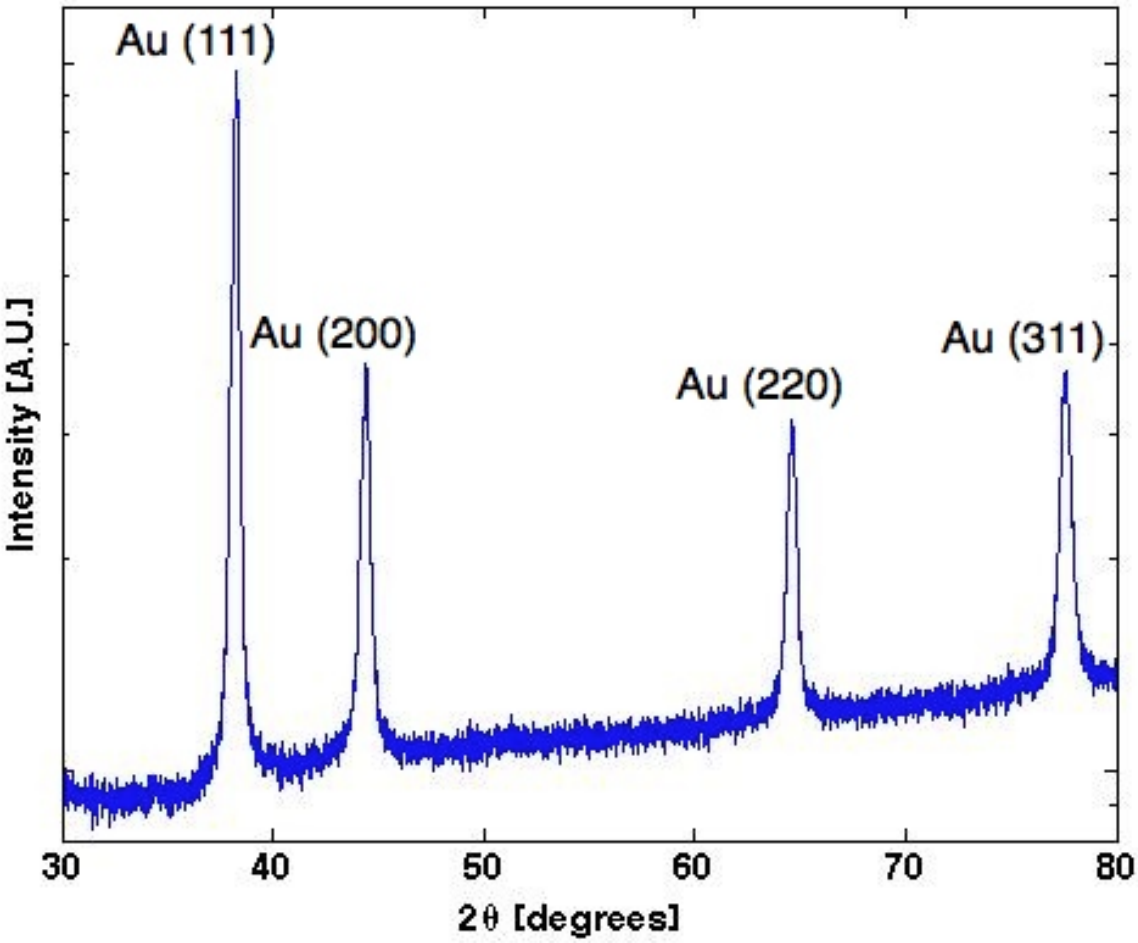

Figure S2. XRD patterns of pristine Au microlattice.

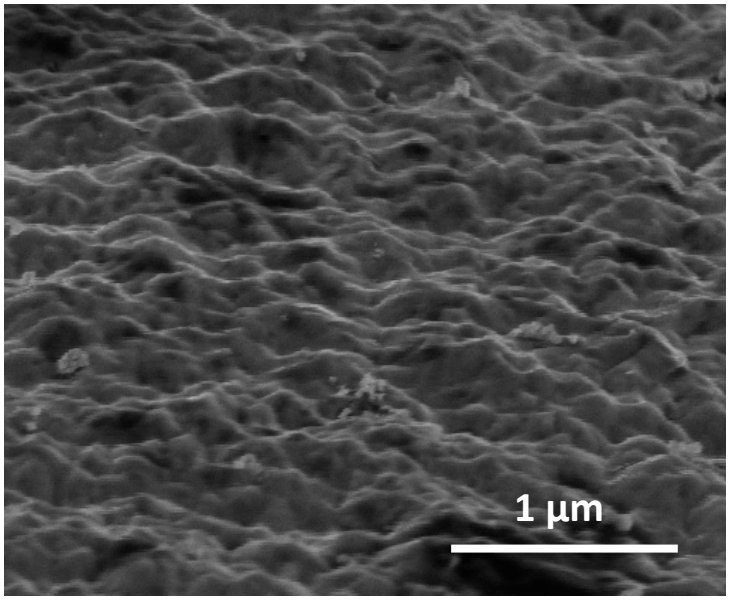

Figure S3. SEM image of the surface of a Au microlattice electrode discharged at 210 nA cm^{-2}_{true}. No noticeable formation of "toroids".

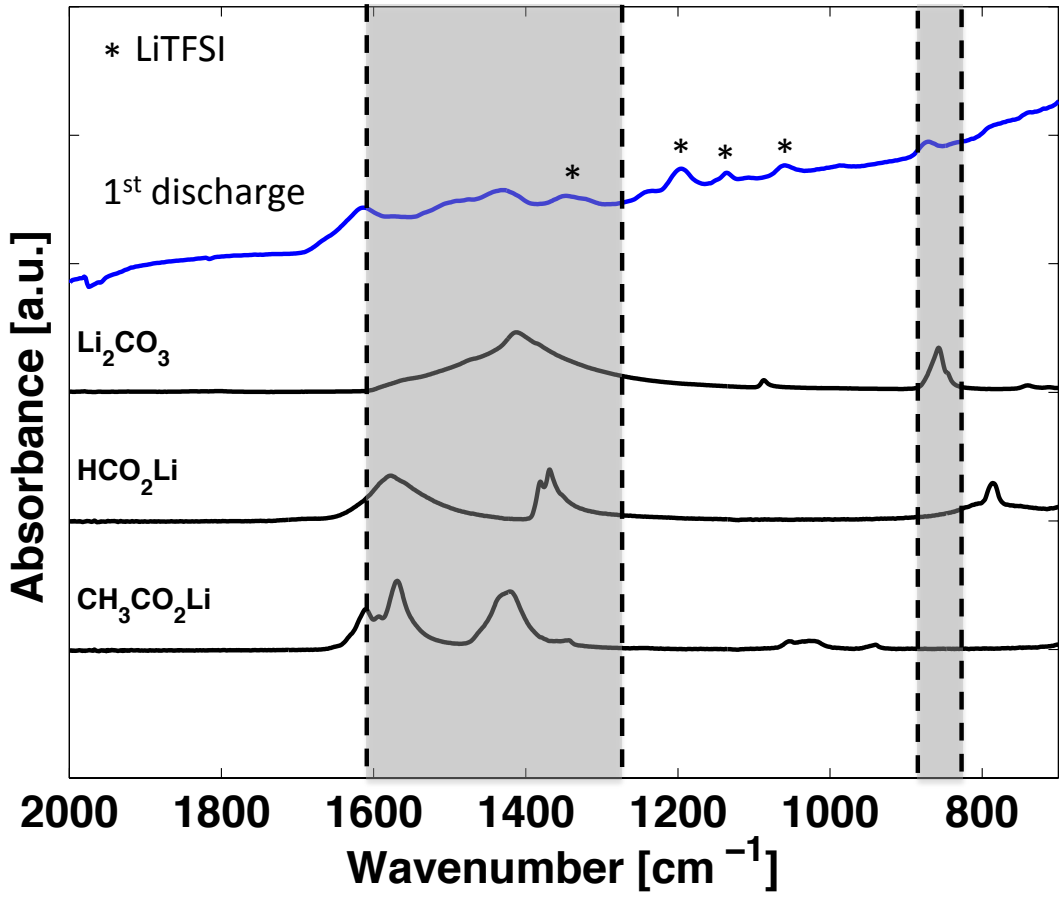

Figure S4. FTIR spectrum of a microlattice after the first discharge, taken in a N_2 glovebox. The grey zone indicates Li_2CO_3 peaks. The peaks at 1340 cm^{-1}, 1200 cm^{-1}, 1136 cm^{-1} and 1060 cm^{-1} denoted by "⁎" are attributed to residual LiTFSI. This sample is not washed prior to characterization. The peak LiTFSI locations are in good agreement with Gowda *et al*[1].

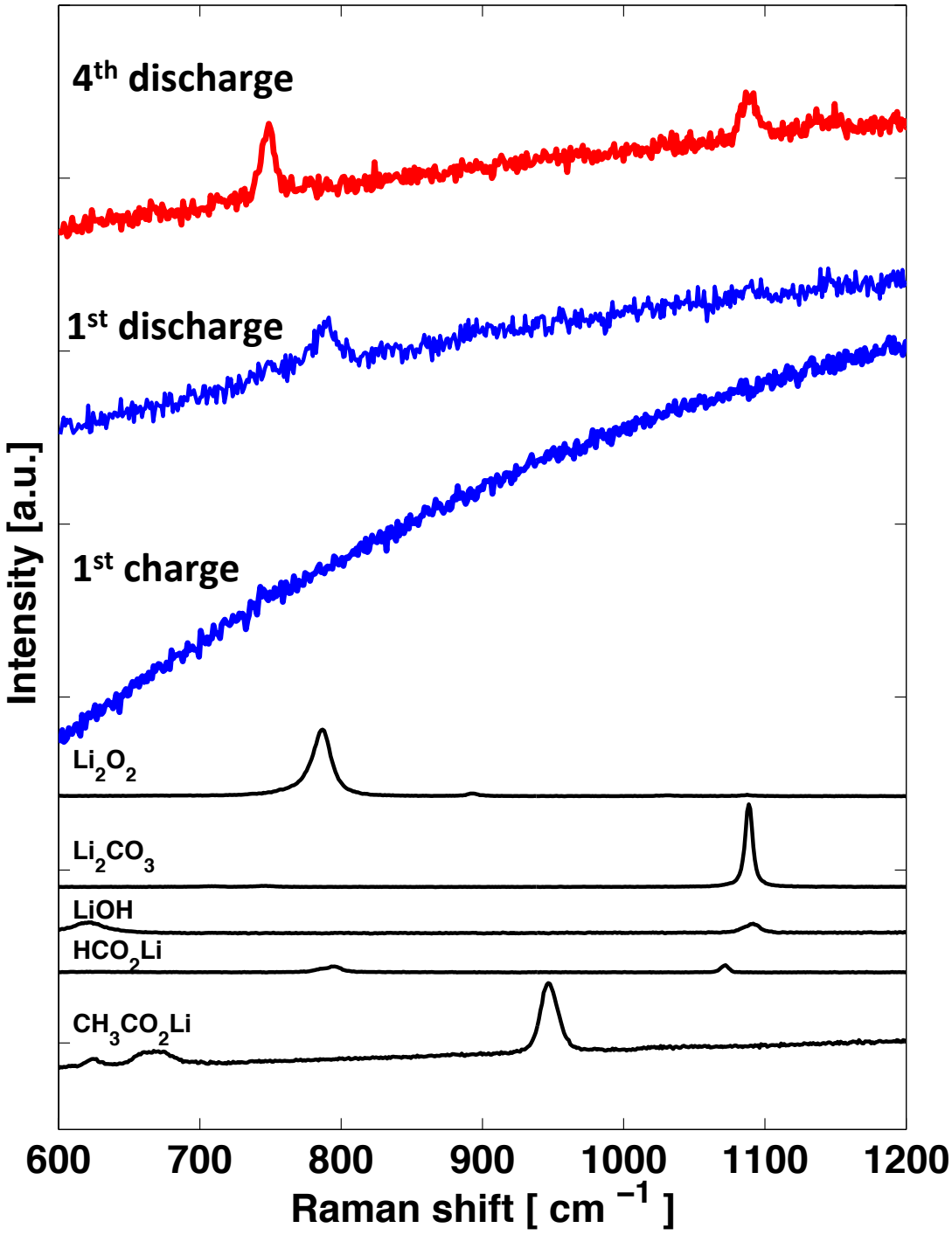

Figure S5. Raman spectra of a microlattices after the 1st charge, 1st discharge, and after 3 cycles ending with a 4th discharge. References obtained from commercially available powders from Sigma Aldrich.

The powder references exhibit peaks at Raman shifts of 790 cm^{-1} and 1090 cm^{-1} for Li_2O_2 and Li_2CO_3, respectively, which agrees well with literature.[2–7] The predominant product after the 1st discharge was Li_2O_2, as indicated by a peak in the Raman data at 790 cm^{-1}. No Li_2CO_3 peaks were observed. The FTIR spectrum showed several peaks centered at 1400 cm^{-1} and 860 cm^{-1}, which suggests the presence of a small amount of Li_2CO_3. This discrepancy between the FTIR and the Raman data may arise from the C–O bond being more infrared active than Raman active.[8,9] The increase in Li_2CO_3 can be readily observed by the emergence of a peak at 1090 cm^{-1} in the Raman data, which was absent after the 1st discharge (Figure 5). This finding is supported by the IR data where the intensity of the Li_2CO_3 peaks increased, along with that of HCO_2Li and CH_3CO_2Li, with cycling.

An interesting featured observed in the Raman spectra showed a peak at 750 cm^{-1}, which does not coincide with the previously observed peak for Li_2O_2 at 790 cm^{-1}, nor does it align with expected side reaction products such has LiOH, HCO_2Li and CH_3CO_2Li. One possibility is that the 750 cm^{-1} peak belongs to Li_2O_2 where the O – O bond strength is different from that of the Li_2O_2 formed on the 1st cycle. Varying positions for the O-O stretch in Li_2O_2 formed during discharge have been reported in literature, with values between 745 cm^{-1} [10] and 808 cm^{-1} [10,11]. The origins of this peak shift remain elusive; several factors that can potentially affect the bonding strength have been proposed, for example the crystallinity of Li_2O_2, which can lead to peak broadening or peak disappearance,[12,13] or hydration of Li_2O_2 , which can lead to a blue shift of up to 70

cm^{-1}.[5,14] It is likely that in this work this shift is caused by the local contamination on Li_2O_2 surfaces from LiOH or other species.

References

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